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A Thesis

MYRISTIC ACID FILMS AT LOW SURFACE PRESSURES

By

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Department of Chemistry.

August 11, 1948.

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This is to certify that the undersigned have read and recommended to the Committee on Graduate Studies for acceptance, a thesis submitted by G.P. Semeluk, B.Sc., entitled

"Myristic Acid Films at Low Surface Pressures"

Professor

Professor

Professor

MYRISTIC ACID FILMS AT LOW SURFACE PRESSURES

Submitted in Partial
Fulfillment

of the

Requirements for the degree

of

Master of Science

by

G.P. Semeluk, B.Sc.

Under the direction of

Dr. J.L. Morrison

Time devoted to this work - 12 months.

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TABLE OF CONTENTS

Introduction 1

General Theory of Insoluble films on Water Surfaces.

1. History 2
2. Spreading 3
3. The Kinetic Picture of the Monolayer 5
4. Limitations of the Analogy 8
5. Myristic Acid Films 12
6. Rubber 13

Apparatus

1. The Horizontal Film Balance 14
2. The Wilhelmy Balance 15
3. Surface Potential System 15
4. Additions and Changes 15
5. Reflux - Fractionating Columns 16
6. Modified Soxhlet Apparatus 16

Experimental Procedures

1. Tray Preparation 17
2. Myristic Acid Preparation 18
3. Solvents 18
4. Run Procedure 19
5. Thiocyanation of GR-S 20

Results and Discussion

A. Myristic Acid Films 25
   1. Films from Petroleum Ether 25
   2. The Island Phenomenon 28
   3. Double Molecules 33
   4. Films from Benzene 36
   5. Films from Acetone-Petroleum Ether 36

B. Solvents 37

C. Thiocyanation of GR-S 39

D. Films of Thiocyanated GR-S 41

Summary 46

Recommendations for further work 46

Bibliography 49

Appendix: A Critical Appraisal of Monolayer Technique.

INTRODUCTION

INTRODUCTION

Although the original intention was to study films of rubber derivatives by means of a film balance, it was soon found that a critical study first had to be made of monolayers at very low film pressures in order to become familiar with the effects of solvents on measurements, and to become acquainted with the characteristics of gaseous films. For this purpose, myristic acid was chosen because of its solubility in the same hydrocarbon solvents used in rubber work, and because it has previously been studied and found to produce gaseous monolayers.

This study of gaseous myristic acid films was confined to molecular areas ranging from 27,000 to 600 square Angstroms per molecule.

GENERAL THEORY OF INSOLUBLE FILMS ON WATER SURFACES

1. History

The existence of monomolecular films, or monlayers, was first postulated by Rayleigh in 1899, to explain a peculiarity in the behavior of a water surface when an oil was spread on it. Both Pockels and Rayleigh had observed that no perceptible lowering of surface tension was caused by a given quantity of oil, provided the area occupied by the oil film exceeded a certain critical amount, but that as the area was decreased below this critical value, the surface tension fell rapidly. Within the next fifteen years more experimental evidence came to light which confirmed this postulate, and the kinetic theory of monolayers was developed.

Monolayers were first studied with a film balance in 1917 by Langmuir (1), who made force-area measurements on oils and the fatty acids. His results led him to deduce the existence of two dimensional states analagous to those in three dimensions. A great many other workers entered this field, contributing new techniques, and adding to the knowledge of the subject. Guyot and Frumkin introduced the determinations of surface potential, and the simultaneous measurement of surface pressure and surface potential was

added by Adam and Harding (2). Long-chain fatty acids and alcohols have been extensively studied by Schofield and Rideal, Adam and Jessop, Harding, Schulman, Harkins and others. Gorter, Philippi, Dervichian, Guastalla, Langmuir, and Bull have studied proteins.

The results of these experiments have assisted greatly in determinations of molecular structure and molecular or particle weight, particularly where conventional methods have failed. The application of the monolayer technique to synthetic rubber research is more recent.

2. Spreading

Three theories have been advanced to explain the spreading of insoluble substances on water surfaces:

(a) Rayleigh believed that only impurities on the surface would prevent spreading.

(b) Langmuir believed that the molecule must possess certain characteristics before it will spread. The molecule must contain a polar or "water-soluble" group to be attracted to the water, and a non-polar group to make it insoluble in water.

(c) Harkins thermodynamic theory, which covers all types

of spreading, states that a substance will spread only if it lowers the free energy of the surface in the process by which it spreads. Whether a monolayer or a duplex film (one in which the upper and lower surfaces have no effect on each other, usually a multilayer) forms depends on which will give the lower free energy. Only a few examples of the duplex film are known. Generally, if a spreading substance is placed on the surface in an amount in excess of the quantity needed to form a monolayer, the excess forms one or more lenses, with the remainder of the surface covered by a monolayer.

Rayleigh's theory has now been discarded to a large extent, while the other two are favored. Experimental results supporting either theory, or the interpretations of these results, often contradict each other. Thus, Adam (4) says that measurements have been made on fatty acids containing from 14 to 34 carbon atoms, while Harkins (3) states, "n-straight chain paraffin acids are particularly non-spreading as monolayers if the number of carbon atoms is much greater than twenty." Some evidence has been obtained in this work which seems to support Harkins' theory.

It appears that both of the latter theories apply for measurements made under the usual conditions employed in

monolayer work. This will be discussed later.

3. The Kinetic Picture of the Monolayer

According to the kinetic theory, the monolayer may be considered as single molecules floating on the water surface, free to move about on the surface, but anchored to it by polar groups. Such a system is, in effect, a two dimensional system. Assuming thermal agitation of the molecules, existence of intermolecular forces and collision diameters, the picture becomes analagous to a three dimensional system. The two dimensional system, then, might be expected to exhibit changes of state, dependent, as in three dimensions, on the properties of the system. Such is found to be the case (figure 1), the intensive properties being temperature and surface pressure, and the extensive property being the area.

The monolayer technique is concerned primarily with measurements of some of these properties, and consists essentially of spreading a substance to a thickness of one molecule on the surface of an aqueous substrate, confining this film to a known variable area, and making two types of measurements on it:

1. Force or surface pressure exerted by this film for

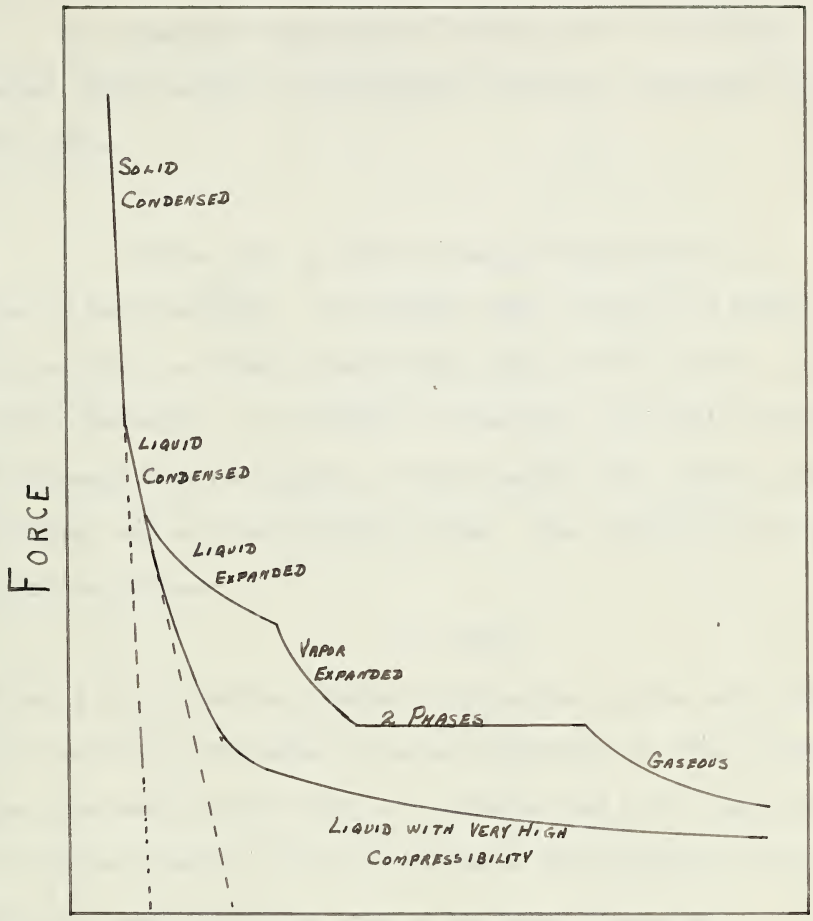


Figure 1

Two Dimensional States - Adam's Classification.

the different areas occupied by it.

2. Potential change across the film for the different areas, which assists in determining molecular orientation in the film.

If the film is dilute enough, it may behave as a gas in two dimensions. In studying such a film it is useful to postulate an ideal gaseous film, just as it is useful, in three dimensions, to postulate an ideal gas. The ideal gaseous film would then be composed of point masses with random thermal motions, and no inter-particle forces. The equation of state might be written

$$FA = nRT,$$

where F is the surface pressure in dynes/cm., A the area occupied by the film, n the number of moles comprising the film, R the gas constant in units which are suitable, and T the temperature in degrees Absolute. The derivation of this equation from the kinetic theory parallels that of its three dimensional analogue(5).

Deviations from the ideal are to be expected, and are found experimentally to be analogous to three dimensional deviations(figure 2). Reasoning similarly to Van der Waals (4)

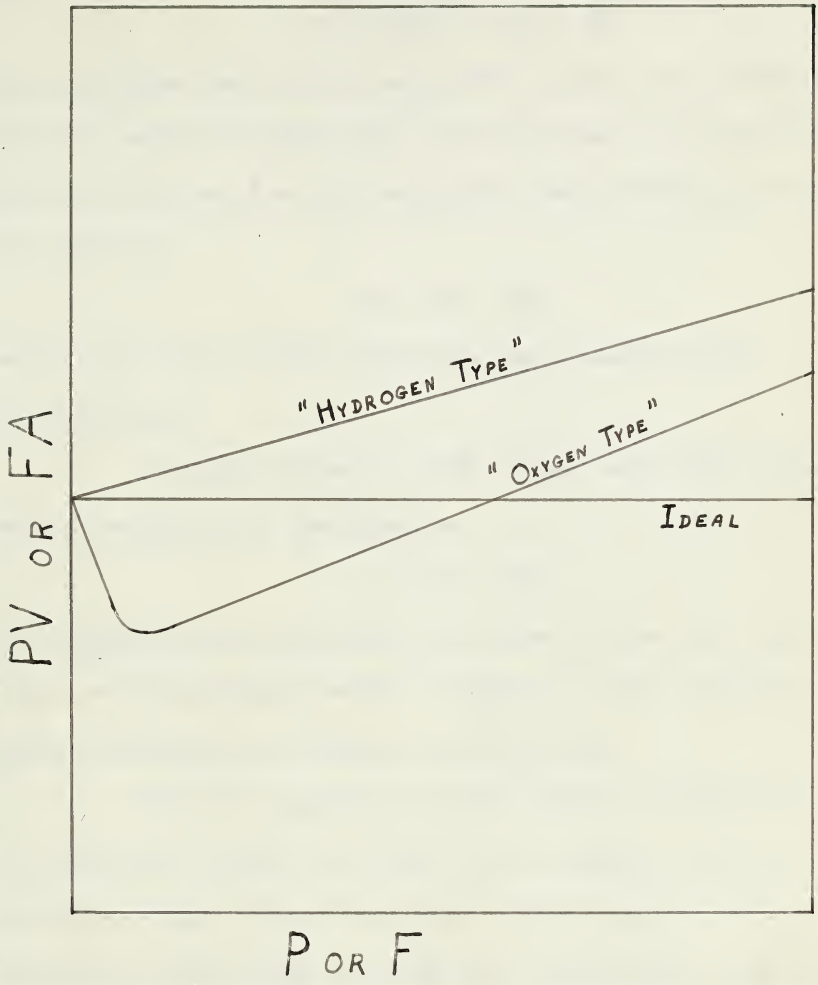


Figure 2

Deviations from Ideal Laws

the corrected equation of state for a real gaseous film becomes

$$(F + \alpha/A^2)(A - \beta) = RT,$$

where A is now the area per mole, α/A^2 is the force of attraction, and β is twice the actual area of the molecule. At very low surface pressures β becomes negligible compared with A, giving the equation

$$FA = RT - \alpha/A,$$

which does apply to fatty acid films at pressures below 0.1 dynes/cm. *

At higher pressures, α/A^2 becomes negligible compared with F, resulting in the equation

$$FA = RT + \beta F.$$

All gaseous protein films which have been studied, and the long chain dicarboxylic acids at moderate surface pressures behave according to an equation of this form. *

These two equations are very useful in determining the molecular weights of surface active compounds of unknown molecular weight. If gaseous films of the compound can be obtained, a plot of FA against F for a considerable range of F will reveal whether the gaseous film is of the "hydrogen type"

* These characteristics have been determined only at temperatures very close to room temperature.

or of the "oxygen type". If it is of the hydrogen type, the intercept of the straight line obtained in plotting FA against F, on the FA axis, divided by RT gives the number of moles in the film; and the weight of substance in the film divided by the number of moles will give the molecular weight. The slope of this line is a measure of the area occupied by the molecules of the film.

Should the film be of the oxygen type, a plot of FA against 1/A for values of F below the inversion pressure is used in a similar manner. The slope of the line in this case is a measure of cohesive forces operating between molecules.

4. Limitations of the Analogy

The analogy between the monolayer and a three dimensional system is, of course, not strictly true. In the analogy, no account is taken of any possible interaction between the film and the underlying water which might cause a change in the surface tension of the water. In the study of monolayers of different substances, exceptions to the simple analogy are well known. Several additional states other than solid, liquid and gaseous exist, and the phase relations in a monolayer are somewhat anomalous when compared to three dimensional

relations. For instance, phase changes in two dimensions are rarely of the first order, and are usually of the second or third order (3).

A simple method of classifying phase changes (3) is to consider the discontinuities in the first, second, and third order partial derivatives of the free energy of the system with respect to the film pressure at constant temperature. A discontinuity in one only of these derivatives means the phase transition is the order of the discontinuous derivative. In more familiar terms, a first order change is one in which there is a discontinuity in the area of the film with respect to surface pressure, with an accompanying latent heat change; a second order change is one in which there is no latent heat change, no discontinuity in the area, but in which there are discontinuities in the heat capacity and in the compressibility; a third order change is one in which there are none of the above discontinuities, but a discontinuity in the specific heat with respect to temperature.

Only one first order change has been observed experimentally. This is the direct transformation of a solid, condensed liquid, or expanded film to the gaseous state. The remainder, which have been proved to exist, are second order

changes, although one third order change is subpected (3). An additional first order change has been reported recently (6).

Harkins considers these apparently anomalous phase relations as characteristic of a two dimensional system: the direct result of the loss of one dimension. Further, he states that the actual existence of transformations of order greater than the first (*) is proof that the binding to the subphase is loose enough to allow observation of the increase in order(6).

Guastalla (7) believes that the presence of a coherent film can increase the surface tension of the aqueous subphase because of the electric field it creates, which would cause a decrease in the measured surface pressure. On the basis of this assumption he proposes an equation of state for a liquid expanded film which contains a term that will take this surface tension change into account. Empirically the term evaluates to $b/A^{\frac{3}{2}}$, where b is a constant and A the area. Further, his observations indicate a proportionality between the coefficient b and the calculated electric moment. His empirical equation fits experimental data on fatty acid films extremely well from a pressure of 0.3 dynes/cm. to nearly 25 dynes/cm. (8).

* Most three dimensional transitions are first order.

What appears to be an extension of Guastalla's hypothesis is derived theoretically by Feng and Band (9). They state, as one of their assumptions, "the interaction potential between the 'liquid ends' of the molecules is equivalent to an 'intrinsic pressure' which has the effect of increasing the surface tension at the interface between parent liquid and the monolayer". The picture of the film is, briefly:

The polar ends of the molecules (termed the "liquid ends") which extend into the surface behave as an imperfect gas trapped in an intrinsic pressure, while the tails of the molecules extend above the surface, and, having less cohesion between them, act as a more perfect gas. It is the attraction between the liquid ends that gives the film its coherence, and the free ends which cause it to behave more like a two dimensional gas than a two dimensional liquid.

For purposes of comparison, the equations are

$$F = kT/A - b/A^{3.5} + c/A^{5.5} \quad \text{(Guastalla)}$$

$$F = kT/(A - A_o) - B/A^{5.5} + C/A^4 \quad \text{(Feng and Band)}$$

where the constants b, c, B, C, are independent of the area and A_o is an area dependent only on the collision cross section of the molecules. At large areas, both equations may be written

$$F = kT/A,$$

which is the equation of an ideal gaseous film. The significance of this is that even if interaction with the subphase exists, gaseous films should still approach the behavior of an ideal gaseous film at sufficiently low surface pressures.

5. Myristic Acid Films

These have been investigated at high pressures in very great detail by Adam and Harkins and their respective co-workers. The results of these extensive studies show that myristic acid films exhibit the expected changes of state (those analagous to the three dimensional changes) and in addition exist in states for which there are no corresponding states in three dimensions. With the exception of the experimental determination of thermodynamic quantities other than pressure and area, studies may be considered completed. On the other hand low pressure measurements on gaseous films, because of limitations of conventional apparatuses and the accompanying experimental difficulties, have lagged far behind. The most recent report concerning low pressure determinations on myristic acid which has come to the attention of the author dates back to 1933 (10). The present investigation was concentrated in the range 0.02 to 0.3 dynes/cm., with the

larger number of determinations made below 0.1 dynes/cm.

6. Rubber

Rubber, both natural and synthetic, is known to be unsaturated, which suggests that polar groups could possibly be added to the molecules to give a product which would spread on an aqueous subphase. This, of course, introduces the possibility of substantial structural changes within the molecule during the process of addition. However, in the opinion of workers at the University of Illinois and the University of Western Ontario, relatively few polar groups per molecule are needed to give a spreading derivative (at variance with Harkins' Theory of Spreading). Therefore, it is felt that the risk of some structural changes is worth taking . Even if the molecular structure is somewhat altered, some elucidating information might still be obtained from measurements made on monolayers of these derivatives.

The polar group which is considered to give the smoothest addition is thiocyanogen. The addition procedure usually followed is due to Pummerer and Stark (11) and Rehner (12). No evidence has yet been obtained by any workers that rubber derivatives form gaseous films.

APPARATUS

APPARATUS

The apparatus used is essentially the same as that described in great detail by J. W. V. Hahn (13) and G. W. Hodgson (14), with a few additions and minor changes; and is now located in a new and much larger laboratory equipped primarily to accomodate monolayer work.

Its main features are:

1. The Horizontal Film Balance

This balance is of the Langmuir-Adam type, with original modifications by Hahn. It measures forces directly by means of a phosphor-bronze torsion wire of suitable diameter. Two sizes of torsion wire were used in the present investigation. One, a 5 mil wire, allowed measurements of forces from 0.005 to 1. dyne/cm. The other, a 3 mil wire, allowed measurements of forces from 0.0005 to 0.1 dynes/cm. The 3 mil wire was not used in the lowest tenth of its range.

Forces are registered by float movements, which are transfered through a lever arrangement to a suitable optical system that magnifies them. This balance is used as a null point instrument.

General Assembly

2. The Wilhelmy Balance, which is a vertical type balance, operates on the principle of vertical displacements of a glass slide dipping through the surface of the substrate. These vertical displacements are actuated by surface tension changes. Movements are magnified by the use of an optical system, forces being determined by scale deflections.

Since this balance does not have the required sensitivity (.05 to 2 $\frac{\text{dynes}}{\text{cm}}$) in low pressure measurements, it was not used in this work, except as a check on the horizontal balance.

3. Surface Potential System.

This is for practical purposes a DuBridge and Brown Amplifying circuit, (15), adapted for surface potential work by a polonium coated air electrode and a calomel half cell (13 & 14).

A minor change was made in the switching arrangement to permit convenient transfer from the coarse to the sensitive galvanometer.

4. Additions and Changes.

A refrigerating unit has been installed to allow better control of temperatures. The thermostating liquid is still tap water, as it has not been possible to obtain ethylene glycol in the quantities needed to make the change over.

A control box with a removable front panel and a hinged top, was built to house the electrical units of the auxiliary control circuits. If any unit should fail, it is a simple matter to re-

Surface Potential Controls.

move the control panel (connection with the units is made through two Jone's Plugs) and swing open the top, leaving the units exposed and easily accessible for repairs. A crude alternating current potential divider (from which the relay currents were tapped) was replaced by a transformer, which gives much better service and is less troublesome.

Provision was made for charging batteries without the necessity of their removal from the circuits, by proper operation of a system of switches.

5. Reflux-Fractionating Columns.

Four of these were constructed, one of which is shown in Fig.(3). These were designed in such a manner that drying of the solvent and fractionating could be carried on without having to change over from a reflux condenser to a fractionating column, the receiver being permanently attached to the column. The atmosphere within the column is kept moisture free by an anhydrite absorber between the receiver and the atmosphere. This is the only direct contact with the atmosphere. The Solvent is displaced from the receivers when needed by air pumped into the apparatus through the drier. Such an arrangement helps to eliminate the possibility of contamination which exists with the usual procedures of refluxing and fractionating.

6. Modified Soxhlet Apparatus (Fig.4)

This was designed primarily for use in rubber work, the purpose being to prevent heating of the extraction chamber by the vapors of

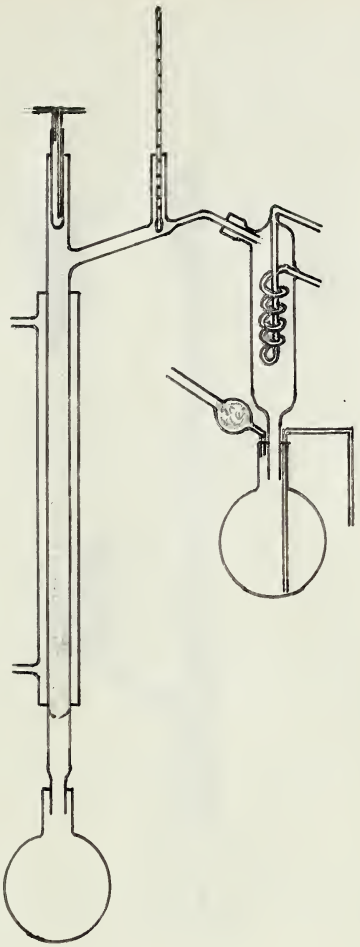


Figure 3

Reflux-Fractionating Column

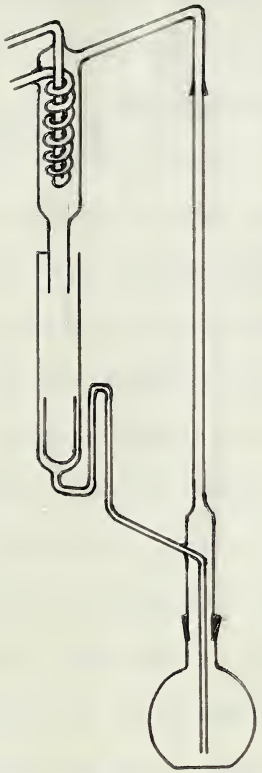


Figure 4

Modified Soxhlet Apparatus

the extracting liquid. There is a possibility of structural changes in synthetic rubber when it is heated much above room temperature, and one of the extracting liquids used in this work, ethanol-toluene azeotrope has a boiling point near 80°C.

EXPERIMENTAL PROCEDURES.

1. Tray Preparation.

The tray is the most important unit in considerations of cleanliness and therefore requires careful attention in its preparation. It is covered with 25 coats of baking type bakelite lacquer (detailed in appendix) for electrical insulation, after the method of McBain and Perry (16), and then scrubbed with boiling distilled water and soap with a final complete rinse with more boiling distilled water. Steam is blown through the false bottom and a petroleum ether (B.P. 40-60 degrees C.) solution of refined filtered paraffin is painted on. The steam line is then disconnected and the tray set in the cupboard to cool, and for the remaining petroleum ether to evaporate. After remaining thus for five or six hours, it is removed and sprayed with a jet of cold distilled water, using compressed air to obtain the pressure, and the adhering droplets of water removed with clean filter paper. It is then carefully placed within the thermostat box and filled to the brim with 0.01NHCL, which is made from conductivity water, and then treated with norit to remove surface active impurities.

The box is then closed and the system allowed to reach equilibrium conditions of temperature and humidity, which takes about five hours. Using the above procedure, which is a modification of that previously

used (14), contamination pressures as low as 0.01 $\frac{\text{dynes}}{\text{cm}}$ at one-quarter compression were observed. Unfortunately this increased within twenty-four hours to the usual level of 0.03 $\frac{\text{dynes}}{\text{cm}}$. For this reason the substrate was replaced once a day with one freshly prepared and cleaned with norit. When replacement of subphase no longer lowers residual contamination, the tray is removed from the box and stripped of its paraffin film by scrubbing with boiling distilled water and soap, and reparaffined as already described. This may be repeated for as long as the lacquer adheres closely to the metal surface, but when a blister develops the lacquer must also be replaced with a fresh coat. (Appendix).

2. Myristic Acid Preparation.

The myristic acid used was from Eastman Kodak. It had a yellowish tinge, so it was purified by recrystallizing from absolute ethanol three times, with norit treatment before each crystallization, then carefully dried. The product gave a sharp melting point at 54°C (uncalibrated thermometer).

3. Solvents.

Petroleum ether, thiophene-free benzene, and acetone were refluxed for 12 hours over phosphorus pentoxide and then fractionated at the rate of one drop per second, in the combined reflux-fractionating columns described under Apparatus. The petroleum ether fraction boiling from 30 to 35°C was the solvent most often used. A fifty-fifty mixture of this with acetone composed the third solvent which was studied.

This solvent is the one used in rubber ~~from~~ studies by the workers at the University of Western Ontario (17).

Solutions of ~~(d) Solutions~~ myristic acid in each of the solvents were prepared in the concentrations:

1. Petroleum ether: 0.0011 mg/ml, 0.0021 mg/ml, 0.0043 mg/ml, 0.0086 mg/ml, 0.0172 mg/ml.
2. Benzene: 0.0035 mg/ml, 0.0070 mg/ml, 0.0140 mg/ml.
3. Acetone-petroleum ether: 0.0034 mg/ml, 0.0069 mg/ml, 0.0138 mg/ml.

To ensure no serious change in concentration of solutions, these were run off immediately after preparation, old solutions being found unreliable.

4. Run Procedure.

The surface was swept 10 times, the balance head lowered and the zero point given time to settle down and become constant. The time allowed for this as determined from a preliminary study of zero point changes, was 10 minutes in the case of the 5 mil torsion wire, and 20 minutes in the case of the 3 mil torsion wire.

Each film was spread at 20°C, drop by drop, over different parts of the surface, from a micropipette delivering 0.0878 ml., on an initial surface of 687 cm^2. A standard 10 minutes, also determined from a preliminary study of spreading times, was allowed for solvent evaporation and spreading of the film. Two types of runs were used: For

all areas below 7000 Å²/molecule, the usual procedure of successively decreasing the surface area available to the film was followed. A hundred runs were made in this manner. For areas above 7000 Å² /molecule each film was spread on different available areas, and only the one initial reading taken. (The balance response was poor when the usual procedure was followed). The surface was then swept and another film spread on a different initial spreading area. This method is very slow and laborious; only one reading can be taken every three-quarters of an hour, while with the other method from 6 to 10 determinations can be made in that time.

Surface potential changes were determined only on the less dilute films, as at very high dilution no change is determinable with the present apparatus. The area probed by the air electrode is less than 1 cm^2, meaning that relatively few molecules are under the electrode to cause a potential change. In addition to this, surface potential measurements made on these films are not very reliable. In spite of extensive shielding of the potential apparatus, any slight variation in the control circuit voltages (110 V.A.C.) causes galvanometer deflec-tions of the same order as those observed on dilute films. The best readings were obtained at night, when voltage fluctuations are not so pronounced.

5. Thiocyanation of GR-S.

The particular synthetic rubber designated "GR-S" is a copolymer of Butadiene and styrene in the approximate proportions six to one.

A sample of this product was obtained from the Polymer Corporation with the intention of converting it into a derivative suitable for monolayer sudy.

Before addition of polar groups is attempted, anti-oxidants, ~~catalysts~~, and emulsifying agents must be removed from the raw product: A Soxhlet extraction thimble is filled with small pieces (4x4x4 mm.) of the sample, placed in the modified Soxhlet, and extracted for at least eight hours with an azeotropic mixture of ethanol and toluene to which 10 % water has been added (18)#. The extracted material is then placed in a Soxhlet apparatus and extracted further with acetone, which removes the ETA and water, facilitating subsequent drying. The final extracted polymer is dried in an Abderhalden vacuum apparatus.

A one percent solution in clean, dry benzene is made immediately after drying, to hinder oxidation by the atmosphere, and this solution is subjected to the addition reaction.

There are two methods used to add the thiocyanate group to a double bond, which will be referred to as "External Addition" and "Internal Addition".

Hereinafter referred to as "ETA".

i. External Addition (17)

2.2 ml. of a 6 % solution of bromine in purified carbon tetrachlor-

ide is added drop by drop to an excess (about 1 g.) of lead thiocyanate suspended in a few ml. of carbon tetrachloride. This addition is made at a low temperature (0 to 5°C.) in such a way that the color of free bromine disappears before more bromine solution is added. The clear liquid separating from the solids is decanted through fine glass wool into 100 g. of the 1% solution of GR-S in benzene. The air above the reaction mixture is flushed out with nitrogen, and the flask with this mixture, stoppered tightly and set in an icebox for eighteen hours. At the end of this time thiocyanogen addition to the double bond is presumably complete.

ii. Internal Addition.

In this method, one gram lead thiocyanate is suspended in 100 g of the 1 % solution of GR-S, and to this is added drop by drop with stirring, 2.2 ml. of 6% bromine in carbon tetrachloride. This mixing is also done at low temperatures, with each fresh addition made only when the solution is again colorless. After removing the air with nitrogen the reaction flask is stoppered and set in an icebox as before. When the reaction is complete, the solution is filtered through fine glass wool to remove the suspended lead salts.

Concentrations of these solutions are determined by eva-

porating 10 ml. aliquots to dryness and weighing the residues. Solutions of concentrations which will give monomolecular films on complete uniform spreading of derivative are then made from the stock solutions. Calculation of these concentrations is based on the assumption of a film density equal to one (20).

The concentrations employed were:

i. Internal addition solutions:

0.967 mg/ml, 0.483 mg/ml, 0.242 mg/ml, 0.121 mg/ml, 0.060 mg/ml,

ii. External addition solutions:

0.763 mg/ml, 0.381 mg/ml, 0.191 mg/ml, 0.095 mg/ml 0.048 mg/ml.

Extent of thiocyanogen addition is determined by microk-jeldahl nitrogen determinations (21) on samples of appropriate volume, both before and after addition. Nitrogen determinations before addition give an indication of the completeness of ETA extraction of the raw product. (Any nitrogen present would be due to the anti-oxidant phenyl β -naphthylamine). For the solutions mentioned above, ETA extraction was considered complete.

RESULTS AND DISCUSSION

Results and Discussion.

A. Myristic Acid Films.

Experiments conducted at very low surface pressures are fraught with difficulties. Only the utmost cleanliness combined with the greatest care can overcome them. Zero point changes, discussed fully in the appendix, may register apparent surface pressures of a greater magnitude than those exerted by the film. Surface contamination in amounts considered negligible at moderate pressures becomes extremely important at low pressures. Rapid, complete spreading, which minimizes the effects of a changing zero and of accumulating contamination, is prevented; and at the same time the float sensitivity is decreased.

Only two-thirds of the runs made on myristic acid films are, in so far as the author was able to ascertain, reliable determinations on the gaseous films. The following discussion is based on these runs.

1. Films from Petroleum Ether.

Measurements made on these dilute films were used in two ways: to find the FA extrapolation value at zero pressure, and to calculate the lateral cohesive forces between the molecules. The assumption was made that at low pressures the film should behave according to an equation of the form

$$FA = \beta - \frac{\alpha}{A}$$

in accordance with deductions made from the analogue of the Van der Waals equation (Introduction). The equation of the best fit straight line was calculated from the experimental measurements by the method of least squates and the constants obtained in the process were correlated with the ideal FA value, and with the "internal cohesion force". It is usually the practice to do this calculation separately for each run. However, this was not done in the present instance. Surface pressure changes with relatively large changes in area are very small at these dilutions, so that only five or six measurements can be taken in the course of one run. For this reason, all determinations in a particular area range were included in one calculation.

Results obtained are divided into two classes according to whether they were determined in a conventional type of run, or single-value runs. The conventional type of run was employed for areas less than 7000 square Angstroms per molecule, using a 5 mil torsion wire; for areas greater than this, a 3 mil torsion wire was used and only one determingtion made on each film, in an attempt to prevent any vibration which might cause a zero point change.

Table 1 summarizes the results.

TABLE 1.

Run type	Nol of Determinations	FA	α
Conventional	59	405×10^{-16} ergs/molecule	5.15×10^{-27} dynecm^3/(molecule)^2
Single Value	29	406 " "	4.31 "
Ideal		402 " "	0

The surface vapor pressure at 20°C was found to be 0.258 dynes/cm, and the transition of gas to liquid began at approximately 700 A^2 /molecule. Comparison with Adams' curves (4) shows that these results are near the expected values for this temperature.

A comparison of the internal forces with those of carbon dioxide, which shows changes of state below 30°C, is possible. Arbitrarily choosing an area of 12,000 A^2 /molecule for myristic acid, the corresponding film pressure is approximately 0.03 dynes/cm.

This pressure is equivalent to a three dimensional pressure of $\frac{0.03 \text{ dynes/cm}}{4.5 \times 10^{-8} \text{ cm}} = 6.67 \times 10^5 \frac{\text{dynes}}{\text{cm}^2}$

$= 6.58 \times 10^{-2}$ atm,

using Adam's method (4) of comparison.

The Volume of one mole of carbon dioxide at this pressure, and at 20°C, is 363.5 litres, from which the internal cohesive pressure is $\frac{a}{V^2} = \frac{3.6 \text{ litre}^2 \text{ atm}}{(363.5)^2 \text{ litre}^2} = 2.73 \times 10^{-5}$ atm.

In the case of myristic acid,

$$\frac{\alpha}{A^2} = \frac{4.31 \times 10^{-27} \frac{\text{dyne cm}^3}{\text{molecule}^2}}{1.44 \times 10^{-24} \frac{\text{cm}^4}{\text{molecule}^2}} = 2.99 \times 10^{-3} \text{ dynes/cm}.$$

In three dimensions this is equivalent to

$$\frac{2.99 \times 10^{-3} \text{ dynes/cm}}{4.5 \times 10^{-8} \text{ cm}} = 6.64 \times 10^{4} \text{ dynes/cm}^2$$

$$= 7.56 \times 10^{-3} \text{ atm}.$$

This value is greater than that for a three dimensional system, in a corresponding state, but is less than internal cohesive forces of liquids, the order of which is from 10^4 to 10^5 atm (22).

The FA values are in good agreement, being only about 1% high. Adam and Jessop (5) reported extrapolation values consistently 25% low at 14.5°C. The phenomenon discussed below may be a partial explanation of their low values.

2. The Island Phenomenon.

For areas less than 6000 Å^2 /molecule, force readings taken at successively smaller areas ten minutes after spreading a film exhibited the strange phenomenon of a lower film pressure at a smaller surface area instead of a greater pressure. This would continue for several decrements of area, thenthe pressure would suddenly rise, and again the same behavior would be repeated. Mapping the surface with the surface potential apparatus qualitatively indicated a non-homogeneous film. Wherever a drop of solution had been placed, the surface potential was 5 to 10

millivolts more positive. Other portions of the surface showed no change from the clean-surface potential. This indicated the presence of islands, which meant that no measurements taken on this film could be considered reliable determinations on a gaseous film. Since the film did not become homogeneous in a convenient lenght of time, a device was employed which improved the conditions. The film was compressed to one-seventh its original area to cause the islands to merge, then it was expanded very slowly (during 10 to 15 minutes). Surface potentials still varied over the surface, but to a lesser extent (2 to 6 millivolts), and nowhere was a clean-surface potential read. It was concluded that the film was much more uniform, and the run was repeated, with more consistent force measurements obtained. This type of behavior was evident with both petroleum ether and benzene solutions. Table 2 illustrates the island phenomenon.

TABLE 2

Rune no. 73 (0.0878 ml. of 0.0043 mg/ml in petroleum ether)

$A(\frac{A^{02}}{\text{MOLECULE}})$	$F(\frac{\text{dynes}}{\text{cm.}})$	$FA\ (\frac{\text{ergs}}{\text{molecule}} \times 10^{16})$
6820	0.045	309
6020	0.097	583
5220	< 0.097	< 507
4410	< 0.097	< 428
3610	0.126	455

2810	< 0.126	< 354
2010	0.172	346

Re- run of no. 73: (after de-compression)

6820	0.045	309
6020	0.052	312
5220	0.058	304
4410	0.068	300
3610	0.074	269
2810	0.091	255
2010	0.113	227

Although the time required to complete a run is increased by this modified procedure, it wasfound that contamination had not increased sufficiently to alter the results.

When the 3 mil torsion wire was used, a few more runs were made in this area range to check on the island phenomenon.

Curiously enough, the effect was not nearly so pronounced, although it still was evident. These check runs were further handicapped by changes of zero induced by vibrations caused on decreasing the areas. It was because of this that the single-value run method was adopted for work on areas up to 30,000 square Ångstroms per molecule. It was found that solutions more dilute than 0.0043 mg/ml apparently did not give rise to islands $\frac{7}{8}$ complete spreading had taken place within ten minutes after the film was pipetted on

to the surface.

Formation of islands is easily explained. Careful observation of the surface during spreading showed that each drop of solution did not form a lens larger than two to three cm. diameter before it had evaporated, leaving behind an island of myristic acid. Immediately after pipetting the solution on surface, the pressure always rose momentarily to a fairly high value (an estimate would be about 0.3 dynes/cm.), which rapidly fell back to zero as the solvent evaporated within a minute, then the pressure rose very slowly for the next few minutes. This confirms Harkins' Theory of Spreading, which requires a monomolecular film of hydrocarbon in equilibrium with visible lenses of liquid. If this is actually the case, then it is not difficult to see that the spreading of the solvent to a monomolecular film of a thickness of 5 to 10 Å would not "drag" many myristic acid molecules along with it, since these molecules are anchoredto the surface. It is more likely that the great majority of myristic acid molecules are concentrated at the site of the lens, and must spread by themselves after the solvent has evaporated.

Erratic force measurements in the presence of islands can also be explained. Each island would have its own pressure, which would be greater than that of the homogeneous film, since the area occupied is much less. The force measured is that exerted on the float. If an island were to come close to the float it would cause a rise of pressure to above that of a uniform film,

depending, of course, on the extent of float length it acted on. If there are no islands in the immediate vicinity of the float, the action would effectively be that of a two dimensional vacuum and cause a low force measurement. It is to be noted that this situation is not the same as that of incomplete spreading caused by contamination. In this case the surface pressure is uniform over the whole surface.

That islands can exist for some time is also easily understood. Thermodynamically, for a substance to spread it must in the act of spreading lower the free energy of the surface (or the surface tension). Kinetically, one would expect the rate of spreading to be directly proportional to the extent of this lowering. If we denote rate of spreading as ds/dt, and change in surface tension as $\Delta\gamma$ (free energy change would then be $\Delta\gamma$ times the area), we could write tentatively

$$ds/dt = k\,\Delta\gamma$$

where k is the proportionality constant. For a lowering of 1 dyne/cm.,

$$ds/dt = k$$

For a lowering of 0.05 dynes/cm. (as at 6800 Å^2 /molecule),

$$ds/dt = 0.05k$$

The area of the available surface is 687 cm^2.

Therefore, spreading time at 1 dyne/cm $= \frac{687}{k}$

Spreading time at 0.05 dynes/cm $= \frac{687}{0.05k}$

Ratio of spreading times $= \frac{687/k}{687/0.05k} = \frac{1}{0.05} = 20,$ #

which means that it would take about 20 times as long for a film to spread at a potential surface tension lowering of 0.05 dynes/cm. than at 1 dyne/cm. In addition, internal cohesion forces are considerable, and this too would tend to hinder spreading. If only 3 minutes were necessary for spreading at 1 dyne/cm (Nutting and Harkins (23) allowed 15 minutes for an area about twice the size of that used here), it would take an hour for a film to spread at 0.05 dynes/cm. The spreading process may be hastened by spreading the solutions over various portions of the surface instead of on one place.

This calculation is not intended to be exact - it is merely an illustration, probably an over-simplification of the real case.

3. Double Molecules.

Moss and Rideal (10), working in the same area range as the author but using a balance employing a vertical torsion wire activated by a couple exerted on the float, have reported a nearly constant value of FA near 200 for gaseous myristic acid films at 17°C. This led them to conclude that the film consisted of extremely stable double molecules instead of as single molecules. These results are contradictory to those reported in this thesis,

but can be largely explained by them. The above authors used a spreading method quite different from that used here. Instead of obtaining successively smaller areas by moving a barrier towards the float, they spread a film from one drop of a solution over the surface, then took a force measurement; another drop was placed on top of the existing film to obtain half the molecular area and again a force measurement was taken. A series of such measurements on films spread one on top of the other comprised their run.

These results were duplicated here to a certain extent (Fig 5), but the author was never able to obtain an FA value near 200 for the first film (spread on a clean surface) in each run. In view of this fact, and the further fact that the island phenomenon disappeared as the areas became much greater than 7000 $Å^2$/molecule, it is possible that the molecules must be within a certain distance of each other before they will spontaneously form double molecules on spreading. This suggests that a critical concentration exists, which is conducive to spontaneous double molecule formation. Since the island phenomenon was most pronounced with the solution of 0.0043 mg/ml concentration, it is believed that this is near this critical concentration. Unfortunately, Moss and Rideal do not report their solution concentration, nor do they give the dimensions and the available surface area of their tray, so that it was impossible to duplicate their procedure exactly. Also, it is not unlikely that temperature is important in the formation of double molecules. Therefore, it seems reasonable to suppose that it

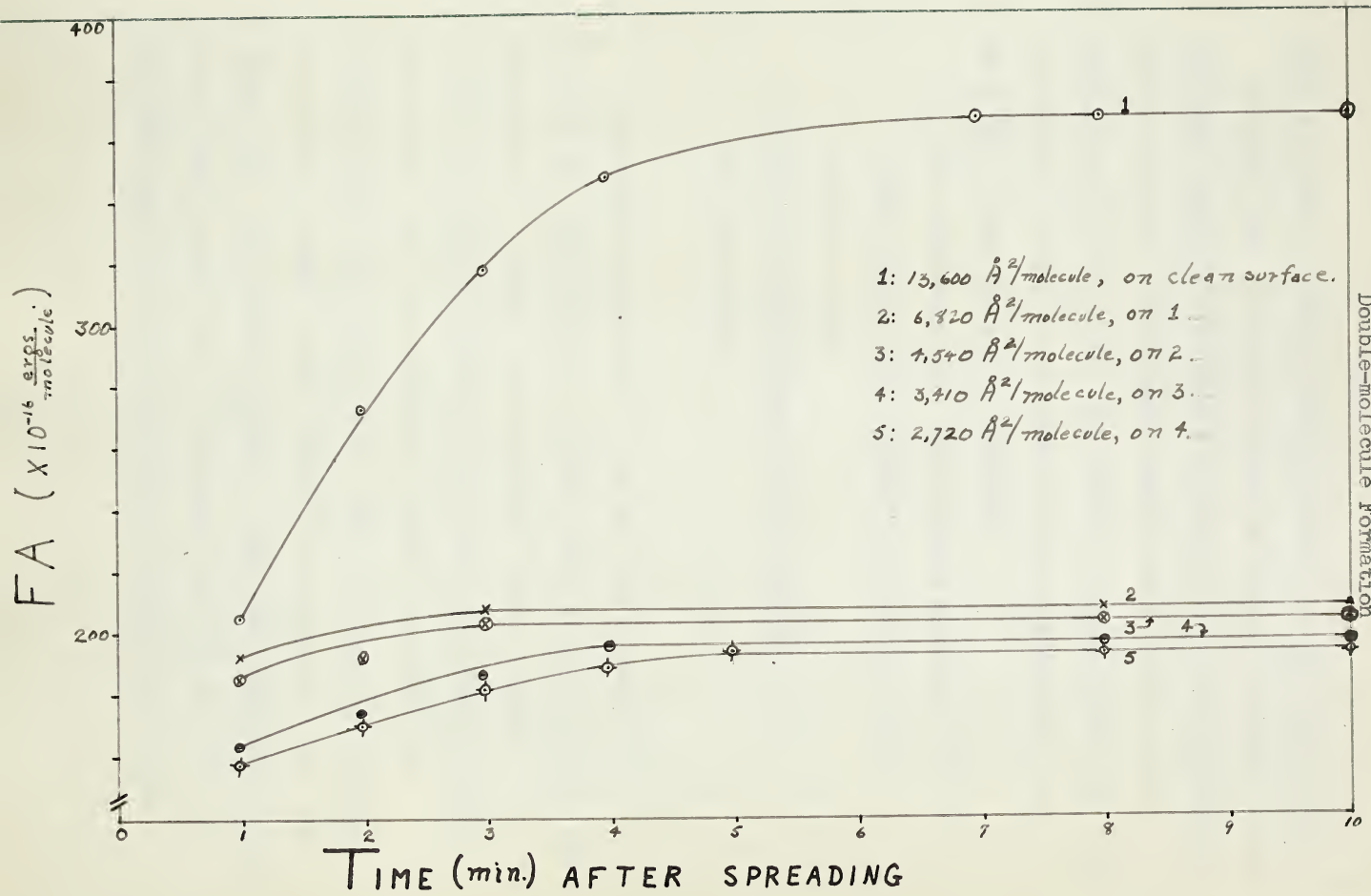

400
300
200
0
1
2
3
4
5
6
7
8
9
10
FA (X 10⁻¹⁶ ergs/molecule)
TIME (min.) AFTER SPREADING
1: 13,600 Å²/molecule, on clean surface.
2: 6,820 Å²/molecule, on 1
3: 1,540 Å²/molecule, on 2
4: 3,410 Å²/molecule, on 3
5: 2,720 Å²/molecule, on 4
Double-molecule Formation

Figure 5

would be easier to obtain double molecules at 17°C than at 20°C.

Assuming that the films obtained by Moss and Rideals' method consisted essentially of double molecules, the measurements were used to calculate the internal cohesive force factor and the extrapolation value of FA. The factor is approximately one fifth as large as for single molecules, and the extrapolated value of FA is 420. These two values indicate:

(1) The double-molecule state behaves much more like an ideal gaseous film at 20°C than does the single-molecule state.

(2) Not all molecules were in the double-molecule state.

The distinct separation of the two sets of results indicates that both states are stable, which further supports the hypothesis of critical concentrations: that is, double molecules would form in the lens before actual spreading occurred. Once either state had completely covered the surface, no further change would take place. This was tested by allowing each state to remain on the surface for over an hour at a constant area. The surface pressure in each case remained constant. It is thus apparent that the sub-phase does have an effect on the monolayer. For single molecules, although the cohesive

forces are great, the surface tension of the underlying liquid is great enough to keep the molecules apart. The double molecules appear to be a stable enough association to resist the tendency of the subphase surface tension to separate them.

4. Films from Benzene.

Because of residual benzene pressure (see under Solvents) measurements made on solutions giving areas greater than 2740 $Å^2$ /molecule are not reliable, and hence are not included in this discussion. At forces greater than 0.1 dynes/cm the films from benzene gave measurements nearly the same as those obtained from petroleum ether solutions. Seventeen determinations in the range 2740 to 1000 $Å^2$ /molecule extrapolated to an FA value of 419, and the internal cohesion factor was calculated to be $5.69 \times 10^{-27} \frac{\text{dyne/cm}^3}{(\text{molecule})^2}$. Both values are higher than those with petroleum ether which is believed due to the increased effect of residual benzene pressure at the larger areas. The area of transition and the surface vapor pressure were the same as for the films spread from petroleum ether.

5. Films from Acetone-Petroleum Ether.

No significant results were obtained from this solvent. In this case the residual pressure was great enough to mask entirely the effects of the myristic acid in the film. FA values were much above 500, and increased with increasing surface pressure instead of decreasing as they normally would. This solvent was

discarded as unsuitable after two runs.

In Figure 6 a summary of the results obtained is shown in a plot of FA against F. The plotted values are sample points to illustrate the distribution about the best fit curves.

B. SOLVENTS

Table 3 summarizes the determinations made on the solvents.

TABLE 3

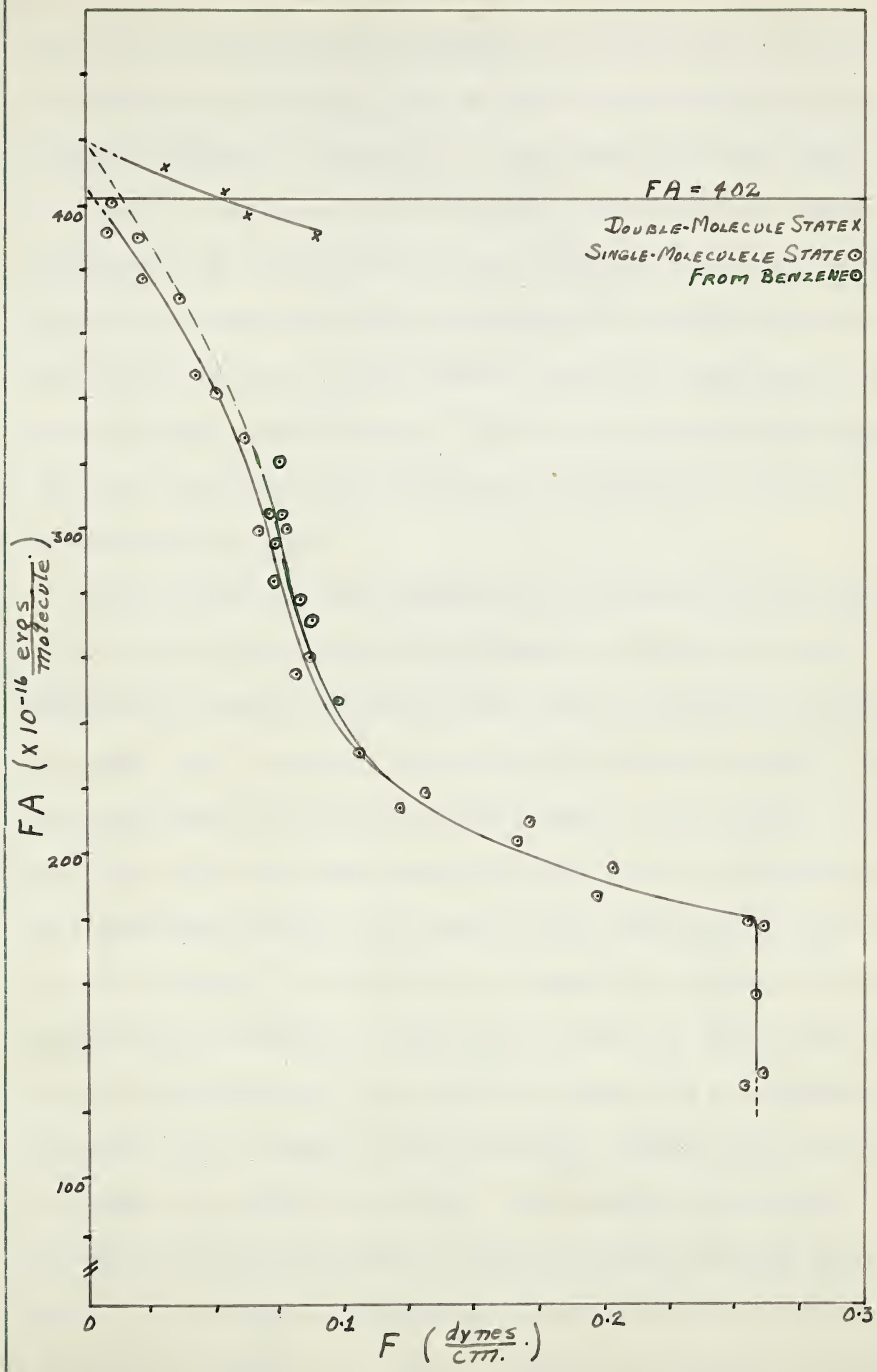
(0.0878 ml. of each solvent was used.)

Solvent	Residual Pressure (dynes/cm)	Surface potential change (millivolts)	Time after spreading
Benzene	0.015	-6	5 min.
	0.0097	-3	10 min.
Petroleum ether (B.P. 30-35°C)	0	?	5 min.
Acetone Petroleum ether	0.162		10 min.
	0.110		13 min.
	0.071		17 min.
	0.071	-5	20 min.

It now becomes apparent why acetone-petroleum ether gave such high values of FA. Since a standard 10 minutes was allowed for evaporation and spreading for every film, acetone-petroleum ether at dilute concentrations contributed more to the measured pressure

Figure 6

Graphical Summary

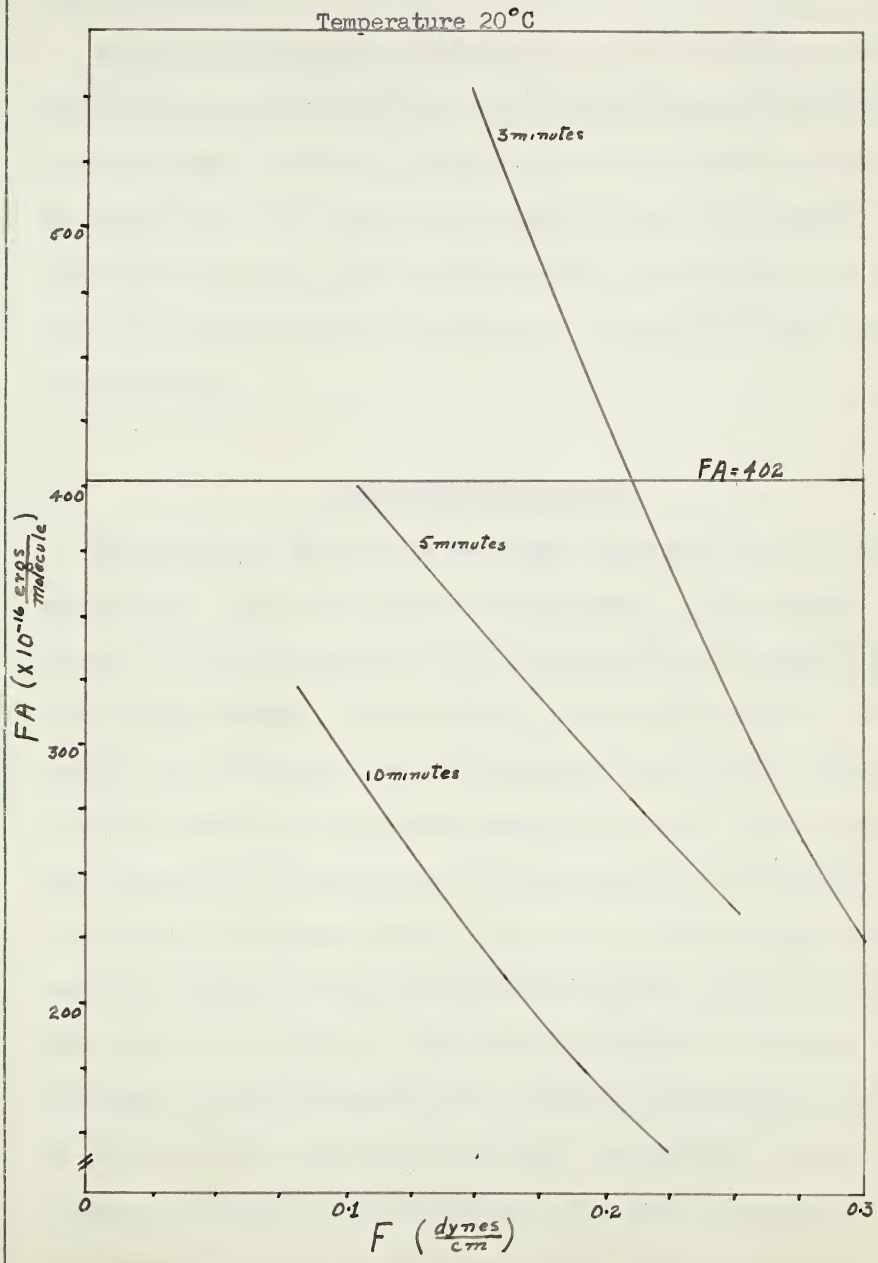


than did the myristic acid monolayer. In the case of benzene the effect of evaporation time on force measurements is illustrated in Figure 7. Actually, it was found that after eight minutes the readings did not vary, but ten minutes was chosen arbitrarily as the evaporation plus spreading time to be on the safe side. Petroleum ether evaporated in a shorter length of time than required to make a surface potential measurement, so that no values were obtained. The full ten minutes were allowed to give as much time for dissipation of islands as could be conveniently allowed.

Each solvent has its disadvantages. Petroleum ether evaporates too quickly, which is conducive to island formation. Benzene and acetone-petroleum ether leave a significant residual pressure, and in addition contaminate the surface quickly. Acetone-petroleum ether is particularly bad in this respect. It was found that after two runs using this solvent the contamination had increased two-fold, and several extra sweepings of the surface would not lessen it. This is to be expected, in view of the great solubility of acetone in water, and it seems to suggest that the acetone concentration in the surface extends for a considerable distance into the bulk of the substrate. Benzene does not contaminate the surface as quickly. Both benzene and acetone-petroleum ether give negative surface potential changes, which makes it impossible to determine the positive surface potential changes of myristic acid films. The surface potential determin-

Figure 7

Effect of Time of Evaporation on Force Measurements
0.0878 ml. of 0.0070 mg/ml. Myristic Acid
in Benzene on 0.01 N. HCl.



ations reported are, therefore, those obtained from petroleum ether solutions.

Referring once again to Figure 6, it is interesting to note that the benzene and petroleum ether curves approach each other as the residual pressure of benzene contributes proportionately less and less to the force measurements. Above 0.1 dynes/cm the curves should be practically identical, since above this value the residual solvent pressure is less than one-tenth the total pressure.

C. THIOCYANATION OF GR-S

Thiocyanation is far from easy even under the best of circumstances. Any trace of moisture or oxygen in the reaction mixture, or over-exposure to light induces polymerization of the thiocyanogen itself. In the case of thiocyanated rubber to be studied as a monolayer, such an occurrence could be the source of a serious error, since polythiocyanagen is itself surface active. The assumption is usually made, by the workers at the University of Illinois and Western Ontario, that all the thiocyanogen adds on to the rubber, and that any polythiocyanogen formed precipitates out of the solution. The possibility of the continued existence of polythiocyanogen as a colloidal suspension in this solution seems to have been overlooked. Accordingly, it was decided to check on this possibility. The tests conducted on two samples, one made by External Addition and the other by

Internal Addition, were:

1. Visual comparison of Tyndall effects to determine the presence and relative amounts of colloids.

2. Centrifuging the samples at 1430xG for 10 minutes, then another comparison of Tyndall effects.

3. Nitrogen determinations twenty-four hours after preparation, and again two weeks later, to determine extent of polythiocyanogen precipitation.

The results are tabulated in Table 4:

TABLE 4

Sample 1 prepared by External Addition

Sample 2 prepared by Internal Addition.

Sample	Conc. (mg/ml)	Attempted $(CNS)_2$ Addition	Apparent Addition	Tyndall Effects
1	7.55	15%	9.8%	intense
2	9.43	15%	2.8%	slight
After two weeks:				
1	7.63		9.0%	intense
2	9.67		2.7%	slight

No. 1 gave a darker yellow liquid than no. 2 within the eighteen hours storage time. Both were apparently clear. However, no. 1 exhibited a very intense Tyndall effect which polarized white light. On the other hand, no. 2 exhibited a slight Tyndall effect of about the same magnitude as the original untreated rubber solution. No. 1 was filtered through fine glass

wool, and then centrifuged at 1430 x G. Neither procedure apparently decreased the Tyndall Effect.

After two weeks nitrogen determinations showed a decrease in apparent $(CNS)_2$ addition in both samples, in the proportions 1/12 for sample 1 and 1/28 for sample 2, suggesting twice as much loss in apparent addition in the first sample. No. 1 showed signs of very slow precipitation of polythiocyanogen on the sides of the flask.

It would thus appear likely that polythiocyanogen is produced as a contaminant during thiocyanation of GR-S, taking the form of a fine colloidal dispersion. If such is the case, any measurements made on thiocyanated GR-S before first removing all the polythiocyanogen would not be reliable. Since polythiocyanogen is so much smaller a molecule than GR-S, it would give a pressure much out of proportion to the actual weight present in comparison with the amount of rubber derivative on the surface.

D. FILMS OF THIOCYANATED GR-S

Measurements made on the two samples of thiocyanated GR-S show an entirely anomalous behavior. Characteristics of this behavior are:

1. Forces measured were functions of the initial spreading area, and not of the area available to each molecule.
2. In every case, and for all concentrations (even those which would give multi-molecular films on complete spreading) the first forces measured were of the magnitude of the residual

benzene pressure which renders them meaningless, and the final ones never were higher than 0.4 dynes/cm, all of them falling between 0.3 and 0.4 dynes/cm.

3. The amount of apparent thiocyanogen addition appeared to have no appreciable affect on measurements. Films of sample 1 and sample 2 exhibited similar behavior.

Visual spreading tests(described in the Appendix) and a comparison with the spreading of myristic acid from similar concentrations confirmed these observations. Unfortunately, it was impossible to make surface potential measurements on these films, as the runs were made at the conclusion of the investigations, and the tray insulation had broken down by this time. Repairs would have required at least two days.

Two interpretations of these results are possible:

1. The rubber thiocyanates did not spread, which would be another confirmation of Harkins' Theory. If it is a fact that thiocyanation does give the polymer the ability to spread, then it may mean that there is no actual addition of the thiocyanogen. Polythiocyanogen may be formed and exist either as a colloid, or as colloidal particles tightly adsorbed to the larger rubber molecules. This would help to explain the yellow color of the addition product. The thiocyanates of isoprene and dimethylbutadiene, closely related to rubber, are known to be colorless, while polythiocyanogen is yellow. In order for the rubber

addition product to have a color, the process of addition must promote the formation of a conjugated double bond system along the polymer chain. The resulting resonance might then give a visible color to the molecule. Although this is not impossible is does not seem likely that addition to an isolated double-bond system should conjugate the unaffected double bonds. That the resonance within the benzene rings contained in GR-S molecules has no effect was demonstrated in the preliminary stages of this investigation: Thiocyanation of natural rubber, which is a polymer of isoprene alone, yielded a similarly yellow "addition product".

2. Spreading does take place, but gives a monolayer of heretofore unknown properties. An extremely coherent film composed of molecules capable of being bent to occupy less area could conceivably behave in such a manner. If the molecules were crowded sufficiently, it is possible that the polar groups could be detached from the surface (since there are relatively few of them in one molecule - only one for every 82 carbon atoms in the chain at 8% addition), and the whole molecule would stand up, remaining anchored to the surface only at one end. This would be much the same as oleic acid molecules which are held flat on the surface by the carboxyl group and the double bond, but stand up when the molecules become tightly packed.

The second interpretation, if it is correct, would confuse attempts to elucidate the structure of rubber thiocyanates. It

would be much easier to determine the structure if the molecule were firmly anchored to the surface.

Since a multilayer of the derivative gave the same range of pressures, it is more likely that the first interpretation of non-spreading is true.

Reports from Western Ontario (20) and Illinois (24) indicate measurements are actually made of these surface films of rubber derivatives. Measurements are made with a Cenco hydrophil balance of a 0.2 dynes/cm sensitivity (25). Since the balance used at the University of Alberta has a sensitivity of 0.005 dynes/cm, it should give more reliable results. However, this may not be necessarily the case, since the concentrations and volumes of solutions used to form a film vary greatly: for monomolecular films of rubber the author uses less than 0.1 ml of solution to minimize the residual solvent pressure, while the others use quantities as large as 5 ml to obtain the same film thickness.

The results of the experiments made here force the author to conclude that thiocyanated GR/S does not spread, at least not under the conditions which were used.

SUMMARY

SUMMARY

It has been shown that the value of FA for a myristic acid film at 20°C and at very low film pressures extrapolates close to the theoretical value of 402 x 10^{-16} $\frac{\text{ergs}}{\text{molecule}}$ if measurements are very carefully made. At the same time it is possible for this film to be made up of double-molecules. Both the spreading method and the concentration of solutions are factors which determine whether the single-molecule or the double-molecule state will be formed. A critical concentration for the formation of the latter state has been postulated, but remains unknown.

The existence of islands in a gaseous myristic acid film has been shown to be both possible and likely, and seems to be related in some manner to the critical concentration for double-molecule formation.

The importance of the type of solvent used, especially in low pressure work, has been established. A water soluble solvent must not be used. Benzene may be used for pressures above 0.1 dynes/cm, but only in very small quantities. The low boiling fraction of petroleum ether is the best at low pressures.

It is doubtful whether thiocyanated rubber prepared by the "External Addition" method is reliable.

All results obtained from films of thiocyanated GR-S indicate that this derivative does not spread.

Recommendations for further work:

1. An attempt should be made to find the critical concentration

for the double molecule state.

2. The double molecule state should be fully investigated.

3. Runs should be made at other temperatures, to determine thermodynamic properties of gaseous films.

4. Thiocyanation of GR-S and other rubbers should be studied.

5. An attempt to add other polar groups to rubbers should be made, e.g., thiol-acetic acid.

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APPENDIX

INDEX

A CRITICAL APPRAISAL OF MONOLAYER TECHNIQUE

Title	Page
A. Sources of Error	
(a) Force Measurements	2
(b) Surface Potential Measurements	5
B. Elimination of Errors of Technique	
(a) Zero Point Changes	6
(b) Cleanliness and Contamination	16
(c) Surface Potential Measurements	24
(d) The Wilhelmy Balance	27
(e) Additional Precautions	29

APPENDIX

A CRITICAL APPRAISAL OF MONOLAYER TECHNIQUE

The following section is intended primarily for those persons who will continue monolayer work in this department at the University of Alberta. Although partly of general interest, the greater part applies to the facilities available in the Chemistry Department. It is written with the hope that the novice may benefit from the results of the author's experience. The recommendations and procedures described below gave the best results, although some may seem to have no logical explanation.

Monolayer study is a fascinating but exacting technique, demanding patience, care, sometimes even endurance, but above all, extreme cleanliness. Reports in the literature give only the slightest hints as to the actual difficulties encountered. The first prerequisite to reliable measurements is to become acquainted with the "personality" of the apparatus. Every sensitive instrument has its own peculiarities, and the film balance is no exception. These peculiarities will be described fully in this appendix.

A. SOURCES OF ERROR

(a) Force Measurements

In the case of force measurements, these are numerous, but may be divided into three classes:

1. Zero Point Changes. This is the most frequent and often the most difficult to correct. At low surface pressures, it is essential that no change in zero take place, otherwise measurements become meaningless.

To check the zero point after completion of a run, move the dial pointer back to the second last reading, increase the area to the second last area reading, move the dial back to the third last reading, increase the area to the third last area reading, and so on, repeating this procedure until the maximum area is reached. At maximum area set the dial at the first reading taken. Wait two or three minutes for oscillations about the wall scale-reading zero to cease, then observe the reading on the wall scale. If this reading has not changed, or has changed very little, consider the run reliable. Hysterisis in the film may change the reading slightly, but this is insignificant in comparison with a change caused by a zero shift. With experience it is not difficult to decide whether a change is due to film hysterisis or to change of zero. It is strongly

recommended that the zero point be checked after each run. This increases the time required for a run, but is worthwhile in the peace of mind that comes from being sure that the forces measured were reliable for that film. Checking the zero point may be omitted for measurements beginning at about 0.3 dynes/cm. This exception applies only when a 5 mil, or larger, torsion wire is used. When using a 3 mil torsion wire always check the zero point.

There are two causes of zero point changes: mechanical and inherent. The mechanical cause and its prevention is outlined below under B.(a). The cause termed "inherent" is due to changes in the substrate level. Most monolayer work is done in a water-saturated atmosphere, and since the substrate is seldom pure water and usually a solution of a salt, the vapor pressure of the substrate is lower than that of pure water. This means there will be a transfer of water to the substrate, which will gradually increase its volume, raising its level, which in turn will raise the float and change the zero point. Fortunately, the error introduced by this cause does not become significant in the time required to make a run. The mechanical causes of zero change, on the other hand, can introduce very serious errors into the force measurements.

2. Non-uniform Spreading. This may take the form of multi-layers, or of a monolayer not completely occupying the whole of the available surface, causing an erroneous area measurement. It can usually be checked with the surface potential apparatus.

It is always good practice to check beforehand the spreading properties of the substance under study. The method used depends on the solvent:

If the solvent is water (as in protein work), sprinkle some lycopodium powder on the surface in a small circle, then place the solution drop by drop in the centre of this circle, and note the time it takes for the film to push the lycopodium to the edges of the surface available for spreading.

If the solvent is a hydrocarbon liquid, spread the solution drop by drop over different parts of the surface between two sweepers, wait a suitable length of time for the solvent to evaporate (5 to 10 minutes), then compress the filmeto one third or one quarter of its initial area. Behind the sweeper which was moved in the compression, sprinkle lycopodium in a line over the whole width of the tray. Carefully remove that sweeper, and note the time it takes for the film to push the line of powdwr to the position the sweeper occupied before compression.

The reason for the different technique with the

hydrocarbon solvents is that the hydrocarbon itself spreads very quickly before evaporation, and in the process scatters the powder all over the surface, making observation of film spreading impossible.

3. Leakage of the Film, past either the float or barrier. This causes a decreasing force reading at a constant area. Dusting a little lycopodium powder behind the float and barrier will detect a leak.

(b) Surface Potential Measurements

When the surface potential apparatus registers inaccurately, it generally does so in such a manner that the readings cannot be confused for reliable ones. Characteristic of faulty behavior are:

1. Frequent and erratic fluctuations in the filament current.

2. Inability to obtain a balance between the plate current and the space charge grid current.

3. Apparent variation in clean-surface potential when the electrode remains stationary. Do not confuse this with a sudden momentary variation caused by line voltage changes in control circuits, which occurs, for example, when the motor of the refrigeration unit

refrigerating unit stops or starts. Turn off the refrigerating unit when taking a reading.

B. ELIMINATION OF ERRORS OF TECHNIQUE

(a) Zero Point Changes

Many of the methodical errors peculiar to the horizontal film balance can be almost entirely eliminated. The most outstanding one, that of zero point shift, was found to be almost wholly due to an absence of equilibrium among torsion wires, the silver lever wires, and the gold ribbons; and an improper balance of pan and counter-weight on the crosspiece suspended by the main torsion wire. The author's laboratory notes show how annoying this can be. In one two-hour study of zero point changes, observations showed that in that time the zero point did not remain constant enough to permit an accurate measurement of even the first force registered ten minutes after spreading. Careful assembly of the balance head prevents such a discouraging situation. The procedure outlined below is both quick and adequate.

In dismantling,

1. Raise the support for the crosspiece (also called levelling device) and clamp the latter in position.

2. Remove the head from the thermostat case, place it on its

stand, and replace the plexiglass front on the case.

3. Detach the silver wire from the crosspiece and then the mirror lever wire from its dural anchor on the float. (Wherever any parts are held by cement, before detaching first melt the cement.)

4. Loosen the main torsion wire, and then the nut which clamps the crosspiece to this wire. Be careful in doing this or the main torsion wire may be broken.

5. Remove torsion wire and crosspiece from the balance head, and place them aside in a manner which will not kink the wire.

6. Loosen the mirror torsion wire, then remove it, along with the mirror, from the head.

7. Detach the gold ribbons from the feet and float and place them in benzene.

8. Remove the legs and stand them up, feet down, in benzene.

9. Detach the dural anchor piece from the float, also the silver wire, and place the float in a wide test tube containing benzene.

The float, feet, and ribbons are prepared by the method described in the section on cleanliness, and then reassembly may

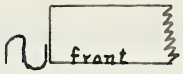
begin:

1. Screw the legs back to the balance head, with the feet pointing inwards, and put the front edges of the feet in line with a ruler.

2. Centre the dural anchor piece on the float (which is set on clean filter paper), then attach it to the float with medium or soft DeKhotinsky cement.

3. Temporarily, place the float midway between the feet, line up its front edge with the front edges of the feet.

4. Smooth the gold ribbons to take out the kinks and other irregularities, then form them into S shapes as nearly identical as is possible. A screw driver stem of appropriate diameter is very useful in doing this. The S's must just fit between the feet and float without undue forcing. This is extremely important, otherwise the float will not stay centred when it is floating on the substrate, nor will it remain in line with the feet, thus causing error in both force and area measurements. Generally, it is impossible to obtain a perfect fit, but the following characteristics are necessary: The top and bottom of the S must be flat and parallel, the two ribbons must be nearly the same shape, and it is better for the S's to be slightly too large than slightly too small for the space.

5. Take the float from between the feet, place it on a piece of filter paper in such a manner that the ends of the float project just beyond the edge of the filter paper. Place a gold against the end of the float with the convex part next to the float and facing front: 

With slightly more than half the width of the ribbon above the plane of the float, cement the S in place with a drop of hard cement. (Hard cement is preferable because it hardens quickly, while soft cements flow too far along the ribbon before they harden, which causes a loss of sensitivity.) Cemant the other S in place symmetrically to the first.

6. Attach a one mil silver wire of sufficient length to the middle of the float,not too close to the front edge.

7. Once again place the float, with the attached gold ribbons and silver wire, between the feet, centre it, and line it up between the feet as before.

8. Approximate the actual level that the float will occupy when on the substrate, raise the feet to the same level by putting blocks beneath them, and cement the ribbons to the feet with hard cement, making certain that the top edge of the ribbons will be horizontal when the float rests on the substrate. This, too, is generally impossible to do the first time, so make

alterations in the positions of the ribbons after observing the way they rest when the head is in position to take measurements.

9. Suspend the mirror from, but do not cement it to, a 3 mil torsion wire; cement a one mil silver wire below, but very close to, the axis of suspension (a third order lever), attach the ends of the torsion wire to the clamps, and tighten the wire.

10. Balance the mirror against the damping vane in such a way that the mirror face is vertical. Drops of cement placed discriminately on the damper or counter-weight is a suitable way to accomplish this.

11. When the mirror is balanced, attach it with soft cement to the torsion wire.

12 Cement the mirror lever wire (one mil silver) to its dural anchor. Be careful here. The attachment must be made in such a way that the face of the mirror is not moved from the vertical to any great extent. Do not attempt to take out the slack in the silver wire, as this moves the mirror face so far from vertical that the zero point will not settle down in a convenient time. The slack in the wire does not interfere with the transference of small movements from the float to the mirror.

13. String the main torsion wire through the hole in the crosspiece, clamp the ends into their holders, and tighten the

torsion wire. Now balance the pan by adjusting the counter-weights. When doing this, be sure that the balance head uprights are vertical: use a level to check this. (When the torsion wire is a new one, i.e., just off the spool, allow it to remain taut in its holders for a few hours before continuing further. This is a good method of straightening kinks and the natural coiling tendency of a new wire. Under no circumstances attempt to straighten kinks by pulling the wire between two finger nails. This only makes matters worse.)

14. Adjust the centre of gravity of the crosspiece until it is just below the point of suspension. This is easily accomplished by moving the nut on the vertical arm up and down. The position of the centre of gravity is decided by watching the swing of the crosspiece. If it swings completely in one direction and does not swing back, the centre of gravity is above the point of suspension. The closer the centre of gravity is to the point of suspension from below, the longer will be the period of the swing.

15. Adjust the bolts on the levelling fingers to give even support to the horizontal arm of the crosspiece.

16. Fix the crosspiece in position first with the levelling device, then with the clamp (or "pliers").

17. Loosen the torsion wire slightly, and tighten the nut

which fixes the torsion wire to the crosspiece. Excessive tightness is undesirable. It leads to a movement of the upright arm of the crosspiece away from the vertical, causing an irregularity in force measurements, and is a source of constant error in the calibration.

18. Now remove any torque which may be present in the main torsion wire as follows: Detach one end of the wire from its holder. Note that the holder has introduced a kink into the wire. Allow the wire to unwind itself, rotate the holder until it fits the kink, and clamp the wire back into the holder. Repeat this procedure with the other end of the wire.

19. Tighten the torsion wire, release the crosspiece, and watch its swing. If it does not come to rest vertically, make adjustments by rotating both holders equally until it does.

20. Raise the levelling device, but do not use the clamping device. Cement the free end of the silver wire, the other end of which is already attached to the float, to the bottom of the vertical arm of the crosspiece. Again, do not attempt to take up all the slack in the silver wire.

21. Release the crosspiece, and watch its swing. If it comes to rest too far from vertical, in the direction of the float, the silver wire is too tight. It is difficult to explain

precisely what "too far from vertical" means. Experience and a study of zero point changes will help to decide this.

22. Raise the levelling device to prevent swinging of the crosspiece during transfer of the head, and replace the head in the thermostat case, in position for measuring. Lower the levelling fingers and allow the balance head to attain thermal equilibrium with its surroundings. This requires about three to four hours. The head itself probably does not take this long to reach equilibrium, but the removal of the plexiglass front allows the atmosphere within the tank to become very much like that of the room. The attainment of constant temperature and humidity conditions does take this long. During this time the zero point changes steadily.

23. Once equilibrium is reached, sweep the surface ten times, raising and lowering the balance head between sweepings to allow any contamination adhering to the float, ribbons and and feet to spread over a cleaner surface and be removed with the next sweeping. It is generally a good practice to have the sweeper behind* the float when the head is lowered and raised,

* "in front of", "the front", denote the direction in which the film lies relative to the object. Thus, the facing edges of the float and barrier are said to be"front" edges. "behind" has the opposite meaning.

as this will tend to prevent accumulation of contamination at tray edges behind the float, where efficient sweeping is difficult. Subsequent forward movement of the sweeper takes the contamination with it. In this way contamination is concentrated behind the barrier, between the sweepers and the end of the tray. *

24. The last two sweepings are managed in this way: Whereas previously each sweeper was dropped behind the float and moved forward (to your right when facing the open side of the tank), the second last is dropped at the opposite end, just in front of the previous sweeper. The balance head is lowered and raised, then the sweeper is moved towards the head until it lies behind the float. The head is lowered and pressed firmly down on the tray (this is necessary because of a peculiarity on the dial side of the head - the main upright on this side will not slide right down to its support unless it is pressed down with the hand. This peculiarity is a possible cause of leaks.). The barrier is then placed in front of the balance head and swept forward until it slips into its place between the fingers of the

* The difference between sweepers and barrier is merely one of length. The barrier is long enough to reach and rest between the fingers of the compressing device. Sweepers are just long enough to rest between the fingers of the sweeping mechanism when they are vertical.

compressing mechanism. The dial pointer is then moved to the right of the zero position, and then brought back slowly to the zero mark.

25. Now move the barrier towards the float and carefully observe its position relative to the tray edges. The fingers should not raise and lower the barrier as it is driven forward. At all times the barrier must rest on both edges of the tray. Any vertical movement of the barrier causes a zero point change and can be the source of a leak.

In connection with this, note that there is an irregularity in the tray edges between the drum readings 340 and 260, which causes a lowering of zero point. This is a constant change, so so that its effect on force readings is easily determined with the dial. Force readings taken in this region must be corrected for the zero point change.

Another peculiarity exists, this time in the fingers which face the plexiglass. Their tendency to rise is compensated for by the use of a counterweight on the horizontal arm.

26. Study the zero point for a period of at least one hour by observing movement of the light spot on the graduated scale, noting especially the changes in the first twenty minutes. It is within the first twenty minutes that the film must be spread if

the effects of contamination falling on the surface are to be negligible during the run.

(b) Cleanliness and Contamination

Quoting G. W. Hodgson (Thesis, 1947), "the need for extreme cleanliness cannot be overemphasised". On cleanliness depends the succes of nearly all determinations made on monolayers. At low pressures contamination may place force measurements in error by 100% or more. Contamination also hinders complete spreading (see photograph, Thesis by G. W. Hodgson, entitled "Film Balance with Talc Boundary".), introducing another error, in this instance, in area measurement. The standard method for determining surface contamination is to compress the "clean" surface slowly to one fourth its original area, and measure the pressure developed. If it is 0.03 dynes/cm. or less, the surface is considered clean. It is difficult to obtain a cleaner surface, but the author did so by modifying the cleaning procedure (main body of this thesis).

A few general remarks may be made concerning cleanliness:

1. Your hands should be washed before each run and shirt sleeves rolled up.

2. Touch nothing with the hands which will later come in contact with the substrate.

3. Keep the inside of the tank clean, put on a few coats of black enamel about once in six months. The time may be determined by the extent of corrosion in the tank.

4. For cleaning sweepers and barrier use only conductivity water which has been treated twice with norit.

5. Cause no excessive jarring of the thermostat box which may shake something from the ceiling on to the surface.

6. Keep lubricants away from the inside of the tank as much as possible, because they too have a vapor pressure, and partially oxidized oils are extremely surface active. If it is necessary to use a lubricant to keep the working parts operating smoothly, use a heavy oil, and use it sparingly.

Preparation of the Tray

The most important unit in cleanliness is the tray, which is prepared as follows:

Scale off the old lacquer, and polish the edges, inside walls, and bottom with fine emery and polishing paper until all dark spots have been removed. Wipe off the grindings with a clean duster, fill the tray with boiling distilled water, scrub it with a clean test tube brush, spill out the water, and rinse

with more boiling distilled water. Turn the tray face down on clean paper and allow it to cool. While it is cooling, mix the bakelite lacquer with its thinner in the proportion 1 to 2 by volume. Although this appears very thin, it was found that it sticks to the metal surface better.

When the tray is cool and dry, with a small paint brush which has been cleaned and soaked in thinner, paint on a thin coat of the thinned lacquer. Make certain there are no air bubbles on the tray, then place in the oven set at 135° C. It is especially important that the first coat have no air bubbles on it.

After a half hour or slightly longer in the oven, remove the tray from the oven, let it cool, apply a second coat with the precaution mentioned above, and again place in the oven for half an hour. This procedure is repeated until twenty-five coats of lacquer have been applied and baked on. It is advisable to keep a log of the number of coats and the times of application. It will be found that only one coat can be baked on in an hour, so arrange to put them on in two series of applications.

Excessive exposure to heat seems to hinder adhesion between series of coats. Thus, the author discovered that if

he painted the coats on in three series of applications (two series of eight coats each, the last of nine coats), the resulting film of baked lacquer scaled off in three layers. When leaving the tray in the oven overnight, turn off the fixed heaters. The twenty-five coats are necessary to ensure a sufficiently high resistance to ground so that the surface potential measurements can be made.

While making runs keep a close watch for blisters in the lacquer. A blister means that the substrate has come in contact with the metal and corrosion has begun. A blister is a seat of contamination and a cause of varying surface potentials. When a blister develops remove the tray from the balance, take off paraffin, scale off all the lacquer and begin as before. Temporary repairs serve to cut down contamination, but do not permit film potential measurements to be made.

When the last coat of lacquer has been applied and baked on, remove the tray from the oven, cool it to room temperature, then place it in the sink and blow steam through the false bottom. Scrub the inside of the tray with boiling distilled water and soap. Rinse with a large quantity of boiling distilled water (6 to 8 litres), then lift the tray out of the sink and allow the remaing water to evaporate. With the steam

still flowing through the false bottom, paint on the paraffin solution, and follow the rest of the procedure as described in the thesis proper.

Preparation of Balance Head Units

The balance head units which come in contact with the substrate must also be treated to prevent them from being sources of contamination. Float, gold ribbons, feet and float cradle are the ones to be considered.

When the float has had all adhering paraffin removed by soaking in benzene, it is rinsed with clean benzene, allowed to dry, then coated with paraffin in the following manner: Holding one end with tweezers, the float is dipped into molten paraffin, withdrawn and moved in such a way as will prevent uneven distribution of paraffin. When the paraffin has hardened, the float is placed on a clean piece of filter paper, picked up at the other end with tweezers and again dipped and withdrawn. When the wax has hardened, the float is ready for attachment.

After the gold ribbons have been formed into the desired shape, they are rinsed in clean benzene, dried, and attached to the float. All handling after the benzene rinse is done with tweezers. When the balance head has been completely assembled, the top edges of the gold ribbons are lightly covered

pure petroleum jelly.

When the paraffin has been cleaned from the feet and legs, and the lacquer scraped off, the feet and legs are rinsed in clean benzene and dried. Five to eight coats of lacquer are baked on the feet in a manner similar to that used on the tray. Then the feet and a half-inch of the legs are dipped into molten paraffin, withdrawn, and the paraffin allowed to harden. They are now attached to the balance head.

The parts of the cradle in the substrate, and for an inch above are also covered with lacquer and paraffin in the same way. The cradle, which supports the float when the balance head is raised, should be only three to four millimetres below the float when it is resting on the substrate surface.

Preparation of Barrier and Sweepers

These are cleaned in hot cleaning solution, rinsed in tap and distilled water, and dried in the oven. Subsequently they are dipped into molten paraffin, holding one end with filter paper between the fingers, Three coats are sufficient. When the paraffin has hardened, the barrier and sweepers are stored in a cylinder of conductivity water until they are to be used.

These items are cleaned immediately before use in a way that does not allow the parts which will later touch the substrate to come in contact with any possible contaminating

agent. They are handled in transfer only at the extreme ends, and when they are removed from the case they are rested, one end on a piece of clean paper, the other end on the edge of a filter paper box, leaving the middle section always untouched. A convenient method of wiping them clean is to pick up a piece of qualitative filter paper by the edge with the left hand, fold it over by manipulation with the fingers of the same hand in such a way as to bring what was the bottom face of the paper to the outside of the fold, and, holding the wash bottle in the right hand wet the paper with norit-treated conductivity water. Setting the wash bottle aside, a sweeper or barrier is picked up by one end with the right hand, the wet part of the filter paper is folded around the sweeper near the end which is held, and the sweeper drawn lightly through the fold. Avoid wetting the filter paper to the extent that the fingers become wet also, and do not use a filter paper more than once. The cleaning is done in one motion, do not rub or hold the paper tightly against the paraffin, because this will rub the contamination into the wax. When there is excessive adherence of water to the paraffin, strip the paraffin off, clean as before and recoat with clean paraffin.

A good plan is to clean and prepare barrier , sweepers

and balance head each time the tray requires cleaning and reparaffing. In this way contamination originating with these items will not nullify the effect of a clean tray.

Preparation of the Substrate

All aqueous substrates are prepared similarly. Use conductivity water to prepare the solution, put in two or three spatulas of norit, shake and let stand for about an hour. Filter through two filter papers (50 cm., folded). Sometimes norit comes through if only a single paper is used. Always invert the filter paper, facing the side, which is exposed in the package, inwards. Two treatments with norit are usually sufficient.

The apparatus for preparing conductivity water is an adaptation of Ellis and Kiehl's. The entering distilled water is preheated by steam to drive off the carbon dioxide, and is distilled from 0.025 M phosphoric acid to remove ammonia. The phosphoric acid should be replaced every three months.

Preparation of Solvents

All liquids used as solvents for substances which are to be studied as monolayers must be free from surface active agents. Conductivity water treated with norit is suitable when the solvent is water. Water insoluble solvents such as the

hydrocarbons should be dried and fractionated immediately before use. This can be done conveniently in one of the reflux-fractionating columns available in the laboratory, and described in detail in the main body of the thesis. Adam and Jessop (5) found that subjecting these dried solvents to chromatographic adsorption did nothing to improve their qualities.

(c) Surface Potential Measurements

In surface potential measurements the most frequent cause of trouble is a breakdown in tray insulation. Therefore, when varying readings on a clean surface are obtained, examine the tray closely: first for blistered lacquer, then for chipped lacquer under the feet. A less frequent source of breakdown is a contact between sweeper fingers and a bare spot on the outside of the tray. When sweeping the surface do not allow these fingers to rub against the sides of the tray, and as soon as sweeping has been completed, turn the fingers away from the tray.

If the trouble is not located in the tray, then check the switches and wiring in the control board. When testing for short circuits, remember that high resistance leaks are detrimental to a D.C. amplifying system, so that in using the ohmmeter to measure resistance to ground, use the range 0 to 250,000 ohms. Remember also that parts of this circuit are grounded. Trace

out the circuit on the wiring diagram, then disconnect at a convenient spot the portion of the circuit being tested from the portion which is grounded.

Fluctuations in the filament current may be caused by either the battery condition or a short in the filament circuit. An over charged battery causes an erratic filament current, but may be safely corrected by discharging it through a three or four ohm resistance for a short length of time. If this does not correct the fluctuations , then look for shorts in the filament circuit.

If it is impossible to obtain a balance between the plate and space charge grid currents, then one or both circuits may have high resistance leaks in them. Look for these first at the soldered joints, where the shielding on the wires may have broken through the insulation.

Complete and detailed wiring diagrams of all circuits, along with operating instructions, are available in the laboratory files. Be sure you understand them completely before you undertake to operate any of them. Some of the parts are expensive and not easily replaced.

Inductive effects, caused by line voltage changes, are easily recognized. They cause the light on the wall galvanometer

scale to move sharply to the observer's left when he is facing the galvanometer, and occurs only when the control grid is in the circuit. This is caused by incomplete shielding of the circuit, but is unavoidable because of the plexiglass front on the case. The laboratory sources of line voltage changes are the intermittent operation of the refrigerating unit, and intermittent currents in the relay circuits. Only the refrigerating unit causes galvanometer deflections serious enough to prevent the taking of a reading.

Check the conditions of the batteries once a week, adding distilled water if necessary. It is not necessary to remove them from the box for recharging, as a switching arrangement for charging is provided on the box. Instructions for this arrangement are also in the files. If batteries are properly taken care of, they will not fail to give a very steady current.

Finally, read the instructions on the data sheet regarding care, installation and operating characteristics of FP-54 electronic tubes. These are very expensive and take a long time to replace.

(d) The Wilhelmy Balance

In contrast to the horizontal film balance, the Wilhelmy is relatively free from peculiarities. The only serious possible source of error is the angle of contact between the slide and the substrate. This must be a zero contact angle otherwise it would be necessary to measure it and make corrections in force measurements.

There are two considerations in obtaining and maintaining a zero contact angle:

1. Cleanliness of the slide.
2. A saturated atmosphere surrounding the slide.

Slides are cleaned as follows:

They are boiled for fifteen minutes in a solution of trisodium phosphate, rinsed with distilled water, and placed in hot cleaning solution for fifteen minutes. After a second rinse in distilled water, they are placed upright in a beaker to allow the excess water to drain off. Grasping them by the thin edges, place them in their holders and stand the whole assembly up in hot cleaning solution, having the cleaning solution reach about three quarters of an inch above the level which the substrate will reach when the assembly is in position for measuring. Rinse the slides with conductivity water after

fifteen minutes of this second cleaning solution treatment, and let them soak in conductivity water of the same depth as the cleaning solution, for at least one hour. Following this, store them in a beaker of 6N NaOH. About five hours before the Wilhelmy is to be used, remove from the base, rinse and soak in conductivity water for one hour, place them in the oven (at room temperature) to dry. Drying them upside down keeps drainage marks away from the parts which will come in contact with the substrate. When the slides are dry they are hung inside the thermostat case to allow them to reach the proper temperature and equilibrium conditions before they are actually used. This eliminates most of the period of waiting for equilibrium conditions if the slides are merely dried and immediately set in place for measurements. The author found that it often took three hours for the slides to reach a constant level in the substrate, if they were not first brought to equilibrium conditions by hanging them in the thermostat box.

It will be found that the slide edges do not wet as completely as the slide faces, because of irregularites in the edges. Although this does not introduce any serious errors into measurements, it can be corrected to a large extent by grinding the slide edges down on some fine emery polishing paper.

In calibration, it is better to remove weights from the left hand pan rather than to add them, because this duplicates the true action of the slides when in use, that is, they rise in the substrate with lowering of surface tension.

(e) Additional Precautions

1. Always be suspicious of a zero point which is very steady and settles down quickly. This is usually a sign that: the mirror counter-weight is resting on the lower one mil silver wire connecting the crosspiece to the float, or this same wire is dipping into the substrate, or the mirror lever wire has broken. Check this always, immediately before spreading.

2. Decide on a spreading method which is suitable for the particular substance, that is, a method which makes the spreading time a minimum, and adopt it as a standard procedure. If other methods are tried, keep the results of these runs separate from the others. They will not necessarily agree.

3. In turning the force dial, rest only your wrist on the case; do not lean against either the case of the concrete block. When operating the compressing device, turn the handles slowly. This will minimize vibrations which are transferred to the float and hinder force measurements. A too rapid turning of handles

also may cause a zero point change.

4. When taking force readings, it is advisable to turn off the stirring motor in the reservoir, as the slight vibration caused by this motor is transferred to the tray and float.

5. Take care of all continuously running mechanisms, especially pump motors. Stirring motor, pump motor, and fans should be cleaned and oiled regularly. A satisfactory cleaning procedure is to soak motors in carbon tetrachloride once a month. Oil them according to instructions in the files. Check the brushes of the pump motor once a week. It does not pay to neglect the auxiliary equipment.

In conclusion, do not be too discouraged if your first runs appear to be failures. Be patient, success will come with experience.

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